

**Authigenic Carbonates from Cold Seep Environments  
at the Cascadia Accretionary Prism, Oregon:  
Archives of Fluid Venting**



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## COMPREHENSIVE ABSTRACT

Authigenic, cold seep-related carbonates are widely distributed in the sediments and on the seafloor of the Cascadia accretionary prism (Kulm et al., 1986). Hydrate Ridge, the crest of one of the accretionary ridges, is known for its cold vent sites where methane-rich, cold fluids and gases emanate into the seawater. On the seafloor, these vent sites are associated with a typical fauna of chemoautotrophic clams (e.g. *Calymene*), surficial bacterial mats (e.g. *Beggiatoa*), sub-seafloor gas hydrates and a variety of authigenic carbonates. These carbonates are not only characteristic for active vent areas. They are also the remnants and witnesses of ancient vents. Therefore, they represent an excellent archive of the age and duration of cold vents, the geochemical signature of the vent fluids and their variability.

Among the different carbonate lithologies, gas hydrate carbonates are the one that are always sampled in direct contact with gas hydrate. These aragonitic carbonates, precipitate in the soft sediment near the sediment-water interface (Bohrmann et al., 1998). Methane, released from destabilizing gas hydrates, is consumed by a microbial consortium of archaea and sulfate reducing bacteria (Boetius et al., 2000) which provides the chemical conditions for carbonate precipitation. Therefore, the gas hydrate carbonates precipitate in direct contact with or even within gas hydrates. The reducing pore water environment in which these carbonates form shows in their low uranium (U) concentrations (mean:  $1.34 \pm 0.35 \mu\text{g/g}$ ) and high  $\delta^{234}\text{U}$  (165 – 317‰). The  $^{230}\text{Th}/^{234}\text{U}$  ages of gas hydrate carbonate samples from the southern Hydrate Ridge range from 0.82 to 6.34 ka. The ages cluster around 1.24 and 4.71 ka. These clusters correspond to periods of intensive fluid flow presumably triggered by tectonic movements, earthquakes or changes in the position of the sealevel.

Another type of carbonates are the also aragonitic chemoherm carbonates which form carbonate build-ups rising above the seafloor by up to 90 m height - so-called chemoherns. These mounds are interpreted to be the above seafloor expression of subseafloor fault systems in cold seep environments. The focused fluid flow through faults creates successively growing chemoherns. A model is proposed that on the surface of the chemoherm carbonates a consortium of anaerobe methane oxidizing bacteria produce a reducing micro-environment enabling carbonate precipitation. Without this micro-environment, aerobic oxidation of methane would rather lead to the dissolution of carbonates than to their formation. The

participation of microbes in the carbonate formation seems to be recorded in spheroidal forms (radius of 250 - 1250  $\mu\text{m}$ ) that might correspond to microbial aggregates and fragmented layers that might correspond to microbial mats. Seawater analyses of water samples taken 5 - 10 m above the vent sites indicate that this seawater is enriched in  $^{234}\text{U}$  ( $\delta^{234}\text{U} = 166 \pm 3\text{‰}$ ) relative to normal seawater ( $\delta^{234}\text{U} = 145.8 \pm 1.7\text{‰}$ ). Therefore, we have named it bottom water. The precipitation of the chemoherm carbonates from bottom water as proposed in the described model is supported by the  $\delta^{234}\text{U}$  values of the chemoherm carbonate samples ( $161 \pm 4\text{‰}$ ) and their comparatively high U concentrations ( $5.52 \pm 0.74 \mu\text{g/g}$ ). A contribution of about 11% of pore water to the bottom water is calculated using a simple box model. The contribution of pore water to the chemoherm carbonates is about 8%. From an averaged U pore water flux ( $32 \pm 16 \text{ ng/cm}^2\cdot\text{a}$ ) and the reconstructed U pore water concentration ( $0.24 \text{ ng/g}$ ), a mean flow rate of  $147 \pm 68 \text{ cm/a}$  can be estimated for the southern Hydrate Ridge area. This value is consistent with previously measured flow rates at Hydrate Ridge ranging from 10 to 1000 cm/a (Tryon and Brown, 2001).

Chemoherm and gas hydrate carbonates form binary mixing lines with the chemoherm carbonates as one well-defined endmember precipitated from bottom water and the gas hydrate carbonates as a second endmember precipitated from pore water with varying admixtures of bottom water.

$^{230}\text{Th}/^{234}\text{U}$  ages from samples of the SE-Knoll chemoherm indicate that this is the oldest chemoherm in the Hydrate Ridge area with a maximum age of  $267.72 \pm 5.49 \text{ ka}$ . The Alvin chemoherm on the northern Hydrate Ridge has been active at least since  $71.96 \pm 0.63 \text{ ka}$ . Ages of samples from a chemoherm on the western flank of the southern Hydrate Ridge, the Pinnacle, range from 7.33 to 11.43 ka. The ages of the Alvin- and SE-Knoll chemoherm samples correspond to time intervals of low sealevel during the glacial climatic stages 2, 4, 6 and 8 and interstadial 7d. The observation that chemoherm carbonates are precipitated during glacial times is supported by the  $\delta^{18}\text{O}$  values of the carbonates which are substantially higher (up to  $5.04\text{‰}$  PDB) than the expected equilibrium value of  $\delta^{18}\text{O} = 3.46\text{‰}$  PDB due to the ice volume effect. The correlation between sealevel and chemoherm carbonate precipitation suggests that the hydraulic pressure difference between the water column and the plumbing system of the chemoherm is one possible mechanism that controls the fluid outflow. In this case, the formation of chemoherms is supposed to be controlled by climatically driven sealevel variations.

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